



Determination of mineral dissolution regimes using flow-through time-resolved analysis (FT-TRA) and numerical simulation



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ABSTRACT

Flow-through time resolved analysis (FT-TRA) involves subjecting small mineral samples (<10 mg) inserted in a miniature flow-through cell (50 μ L) to controlled flows of eluent analyzed on-line by ICP-MS. In this study, FT-TRA is used to empirically determine the dissolution regimes for the two well-studied minerals forsterite and calcite, representing minerals with relatively slow and fast dissolution kinetics. A proportional increase in steady-state effluent [Mg, Si] concentrations with increasing flow-through cell eluent residence times confirms a dominantly surface-controlled dissolution regime for a powdered forsterite sample at pH 2.3, implying that transport limitations are negligible. In contrast, the relationship between flow rates and dissolution rates for single grain calcite samples at pH 2.3–4 reveals that transport limitations affect the rate of calcite dissolution. To provide a quantitative and process-based assessment of the effect of diffusive transport limitations, simulations of the calcite experiments were performed with a high resolution, pore-scale model that considers the geometry of the calcite grain and the FT-TRA flow-through reactor. The pore-scale model reproduces the observed effluent [Ca] concentrations for all experimental conditions using a single set of surface kinetic parameters, by accounting for the formation of a diffusive boundary layer (DBL) that varies in thickness as a function of flow rates. These results demonstrate that combining FT-TRA with pore-scale modeling makes it possible to obtain unprecedented insights not achievable by either method separately, including quantification of DBL thicknesses and the determination of transport controls as a function of pH, flow velocity and residence times.

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1. Introduction

1.1. Dissolution regimes

Accurately predicting mineral dissolution rates is essential for the investigation of many processes in environmental geochemistry, material science, and a wide range of related fields. One approach to reach this goal has been to measure mineral dissolution rates in laboratory experiments, from which dissolution rate parameters can be deduced and then used to predict rates of mineral dissolution under a wide range of conditions (e.g. White and Brantley, 1995). To obtain meaningful dissolution rate parameters that can be applied to a range of environmental conditions, experiments are normally designed to quantify surface-controlled dissolution rates, i.e. the intrinsic rate of detachment of dissolving species from the surface of the mineral (e.g. Berner, 1978; Compton and Unwin, 1990; Morse and Arvidson, 2002; Morse et al., 2007). However, rates measured in laboratory experiments may be affected by the hydrodynamic conditions under which the dissolution

measurements were conducted (e.g. Sjöberg and Rickard, 1984), and thus may not be readily transposed to other conditions or compared between minerals and even mineral crystallographic surfaces.

When a mineral comes into contact with a fluid, a diffusive boundary layer (DBL) forms at the mineral-fluid interface, and dissolution occurs in two distinct steps: first the dissolving species must detach from the surface of the mineral, and second, they must diffuse through the DBL to the bulk solution (e.g. Morse and Arvidson, 2002). The slower of these steps controls the rate of mineral dissolution (e.g. Berner, 1978). When the dissolution rate is limited by the rate of detachment of dissolving species from the surface of the mineral, dissolution is “surface-controlled”. When the dissolution rate of a mineral is limited by the rate of diffusion of dissolution products or reactants across the DBL, dissolution is “transport-controlled”, often significantly limiting the progress of mineral dissolution at the mineral surface.

Under a surface-controlled dissolution regime and far-from-equilibrium conditions, rates of mineral dissolution can be described with rate laws of the form (e.g. Lasaga, 1998):

$$R_{\text{surface}} = \left(\frac{m}{m_0}\right)^{2/3} \sum_{i=1}^{N_p} k_i a_i^{n_i} \quad (1)$$

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where R_{surface} (moles $\text{m}^{-2} \text{s}^{-1}$) is the surface area normalized, surface-controlled dissolution rate, the $(\frac{m}{m_0})^{2/3}$ term accounts for surface area loss over the course of a dissolution experiment, where the exponent 2/3 is applicable for uniformly dissolving spheres or cubes (e.g. Appelo and Postma, 2005), N_p is the number of parallel reaction pathways, k_i (moles $\text{m}^{-2} \text{s}^{-1}$) is the dissolution rate constant for the i th reaction pathway, a_i is the activity of the i th species, and n_i is the reaction order of the i th pathway.

Under a transport-controlled dissolution regime, the dissolving species build up in a diffusive boundary layer (DBL), and Fick's law dictates the rate of diffusion of products or reactants across the DBL (e.g. Lasaga, 1998):

$$R_{\text{transport}} = k_t (C_{\text{surface}} - C_{\text{bulk}}) \quad (2)$$

where $R_{\text{transport}}$ (moles $\text{m}^{-2} \text{s}^{-1}$) is the surface area normalized diffusion rate across the DBL, k_t ($\text{m} \text{s}^{-1}$) is the transport rate constant (with $k_t = D/\delta$, where D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of the dissolved species, and δ (m) is the DBL thickness), C_{surface} and C_{bulk} (moles m^{-3}) are the concentration of the dissolved species in contact with the surface of the mineral and in the bulk fluid, respectively.

1.2. Dissolution regimes as a continuum

In natural and engineered systems, evolving flow conditions may alter the balance between surface-controlled and transport-controlled dissolution kinetics. For a given mineral, the dissolution regime may shift from surface- to transport-controlled as the DBL increases in thickness, and vice versa, if the DBL thickness decreases. Similarly, under given hydrodynamic conditions, the dissolution regime may shift from surface- to transport-controlled as the rate of mineral dissolution increases.

When minerals dissolve, dissolution products detach from the surface and diffuse toward the bulk solution. It is important to note that at steady state, the rate of detachment must be equal to the rate of transport away from the mineral surface by diffusion. If the rate of detachment is slow, the transport rate is equally slow, and can be sustained with a small concentration gradient across the DBL. These conditions imply that the concentrations of dissolution products at the mineral surface are nearly equal to concentrations in the bulk solution. Under these conditions, the rate of dissolution is dominated by the detachment reaction at the mineral surface and is commonly referred to as surface-controlled. The relatively slow rate of detachment from the surface is not significantly affected by concentration build-up near the surface as a result of transport limitations. On the other hand, for minerals dissolving rapidly, the rate of transport must be equally rapid, which can require large concentration gradients across the DBL. Under these conditions, concentrations of dissolution products at the mineral surface tend to differ significantly from the corresponding concentrations in the bulk solution, in particular if the DBL is relatively thick. DBL thickness is affected by hydrodynamic flow conditions at the pore scale, with slower flow velocities resulting in a greater DBL thickness. In the extreme case, the concentrations of dissolution products approach saturation at the mineral surface, driven by the need to increase the diffusive flux away from the mineral surface. Under these conditions, transport limitations result in a decrease in the detachment rate due to near-equilibrium conditions at the mineral surface, and the dissolution rate of minerals is referred to as transport-controlled.

Notably, the two end-members described above (transport-controlled when $C_{\text{surface}} = C_{\text{saturation}}$; surface-controlled when $C_{\text{surface}} = C_{\text{bulk}}$) can only be approached but never reached, otherwise dissolution would stop. Instead, the dissolution rate is always controlled by a continuum between these two extremes. In all steady-state mineral dissolution situations, the rate of detachment must be lower than, but can be infinitesimally close to, its full potential, which is described by

Eq. (1) with activities of the bulk solution. This situation results in an essentially surface-controlled dissolution regime. Likewise, the rate of transport cannot reach its full potential described by Eq. (2) for $C_{\text{surface}} = C_{\text{saturation}}$ but can be infinitesimally close, resulting in an essentially transport-controlled dissolution regime. Between these two extremes, both the detachment rate and the transport rate are lower than their full potentials as the dissolution regime transits between surface- and transport-controlled.

Describing a system as surface- or transport-controlled thus requires an arbitrary subdivision of this continuum. Recently, Rimstidt (2015) proposed to make this distinction by using the diffusive Damköhler number:

$$Da_{II} = R_{\text{surface}}/R_{\text{transport}} \quad (3)$$

where R_{surface} is the rate of detachment at its full potential (as $C_{\text{surface}} \rightarrow C_{\text{bulk}}$) and $R_{\text{transport}}$ is the rate of transport at its full potential (as $C_{\text{surface}} \rightarrow C_{\text{saturation}}$). When $R_{\text{surface}} > 10 \times R_{\text{transport}}$ (i.e. when rate calculated with Eq. (1) $10 \times$ rate calculated from Eq. (2) with $C_{\text{surface}} = C_{\text{saturation}}$), the dissolution regime is deemed surface-controlled, while $R_{\text{surface}} < 0.1 R_{\text{transport}}$ indicates transport control. Because the transition between the two regimes is gradual and the end-members are never truly reached, an alternative to predicating arbitrary cut-offs would be to simply report the value of the diffusive Damköhler number of the system to provide a sense of how far it is in one or the other regime (i.e. large Da_{II} toward surface controlled vs small Da_{II} toward transport controlled), similar to the approach proposed by Raines and Dewers (1997a, 1997b). However, in practice, the DBL thickness is often not constant across the mineral surface, the gradient across the DBL is not linear due to the fact that flow velocities gradually increase toward the bulk solution, and equilibrium concentrations for a given ion ($C_{\text{saturation}}$) can also vary over the mineral surface. As a result, Damköhler numbers must vary over a dissolving mineral surface and their calculation may be complex. Empirical determinations of dissolution regime may thus provide a more practical approach.

1.3. The need to establish a dissolution regime

Because intrinsic mineral dissolution rate parameters must be measured under surface-controlled conditions (e.g. Compton and Unwin, 1990), it is important to establish the dissolution regime under which dissolution rates of minerals are measured before interpreting or using the results. Many of the studies addressing mineral dissolution kinetics rely on measuring bulk solution concentrations to estimate mineral dissolution rates (e.g. Plummer et al., 1978; Plummer et al., 1979; Sjöberg, 1978; Sjöberg and Rickard, 1983, 1984). With the development of high-resolution imaging techniques such as Atomic Force Microscopy (AFM) and Vertical Scanning Interferometry (VSI), some of the focus has now shifted from bulk solution measurements to variations in nano-scale surface topography to estimate mineral dissolution rates of the more soluble minerals (e.g. Liang and Baer, 1997; Arvidson et al., 2003; Ruiz-Agudo and Putnis, 2012). Using this approach, dissolution rates are estimated from volume of mineral loss to dissolution per unit time, converted into moles s^{-1} using the molar volume of the mineral. Although this approach is fundamentally different from the methods using bulk solution composition, it also requires knowledge of the dissolution regime to interpret the data. Thus, a need exists to develop methodologies to determine the rate-limiting dissolution regime when measuring mineral dissolution rates, regardless of which technique is employed to quantify the surface-controlled mineral dissolution rates.

1.4. Previous approaches to determining dissolution regime

The need to determine the rate-limiting mineral dissolution step was quickly identified when studying the rate of dissolution of more soluble minerals such as calcite (e.g. Plummer et al., 1978, 1979;

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